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TITLE: E-BEAM-INDUCED FLUORESCENCE OF EXCIMERS IN CRYOGENIC SOLUTIONS

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E-beam-induced fluorescence of excimers in cryogenic solutions

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Abstract

We have detected the fluorescence emitted from excimer molecules formed in e-beam-pumped mixtures in a liquid argon host. The mixtures were both binary (halogen donors in the liquid argon) and ternary (dilute concentrations of donors and other rare gases in the liquid argon). Many excimers were observed, including the rare-gas dimers Xe_2, Kr_2, and Ar_2. Strong fluorescence was seen from XeF, XeCl, and ArO.

Introduction

Excimers, which are molecules with unstable ground states, are of great interest as lasing species.[1] Dimer excimers such as KrF, XeCl, and XeF are routinely used in uv lasers, and trimers such as Kr_2F and Xe_2Cl are extending the range of excimer lasers into the visible. We have initiated a study of e-beam-pumped solutions of various halogen donors and rare gases in liquid argon; during irradiation these solutions form excited excimers in the liquid. There are several motivations for investigating these excimers. An obvious one is the possibility that liquid excimer lasers might be a great deal more compact than the present gaseous lasers. An equally valid reason is that in solution the excimers are strongly red-shifted, so that lasers at new wavelengths become possible. These large solvent shifts are illustrated by data for the D-X transition of XeF in Table 1.[2] As the atomic weight of the solvent increases, the energy levels are brought closer together, so that the energy of this transition decreases, and the wavelength of the emitted light red-shifts to increasingly larger values. The energy shifts are so large that every solvent change takes this same excimer transition into an entirely new wavelength span.

We report here the initial stage of a systematic investigation of liquid-argon-based binary and ternary systems, in which we detected the created excimers by their optical fluorescence. The halogen donors we used were O_2, N_2O, F_2, NF_3, and Freon-11 (CCl_3F, a Cl donor). In ternary mixes we also added the rare gases Kr and Xe to the Ar host. Most of the expected excimers were formed, those based on Kr being the least successful. Among the brightest were the rare gas dimers themselves, notably Xe_2.

Table 1. Solvent Shifts [Example: the XeF(DX) Transition]

Medium	Wavelength
Gas	264 nm
Liquid argon	282 nm
liquid krypton	312 nm
liquid xenon	371 nm

Apparatus

Figure 1 is a schematic of the apparatus in a plan view. The heart of the system was a liquid-nitrogen-cooled optical cell in which the gas mixtures were liquified. This was surrounded by an evacuated jacket which is not shown. The temperature was controlled by balancing radiation input against cold nitrogen vapor flow, with a resultant stability range of ±2°C.

The 40-ns, 1-MeV e-beam was generated by a commercial Febetron.[3] The energy deposited in the medium through the nickel foil was typically 0.25 J. The penetration depth in the liquid was about 1.5 mm. The other beam dimensions were 19 mm (width) and 3.2 mm (height), giving an active volume of 0.1 cm^3, an energy density of 2.7 J/cm^3, and a power density of 70 MW/cm^3.

The windows on the optical cell were sealed with Pb(Ca) alloy gaskets compressed by the windows onto the flat diamond-turned surface of the cell. The emitted fluorescence escaped into the evacuated optical box through a pair of MgF_2 windows (the second one on the vacuum chamber), and immediately encountered a collimating lens. The edges of the now-collimated beam were diverted by adjustable pick-offs to a pair of photodiodes, one sensitive at 110-330 nm ("vuv photodiode") and the other detecting 250-850 nm ("visible PD"). Because the long e-beam pulse obviated accurate lifetime measurements, no kinetic data are included in this report. The central portion of the beam impinged upon the slit of the vacuum spectrometer. In most of the spectra presented here, a 300-line/mm holographic grating was employed. The spectral detector was an intensified diode array, modified for vuv use by replacing the window before the microchannel-plate intensifier (normally quartz) with a MgF_2 window. The diode array signals were converted into spectra by an accompanying optical multichannel analyzer.[4]

The purity required of the gases and the system was quite stringent. After observing initially inconsistent results, we came to realize that donor (and inadvertent donor) levels on the order of 10 ppb could create spurious spectra; other unidentified contaminants at the same levels quenched the fluorescence completely. After employing a Hydrox gas purifier to clean up the argon[5] and paying scrupulous attention to system cleanliness, these problems were controlled. The gas-handling system was bakeable, compatible with fluorine passivation, limited to 1000 psi, and evacuable to 10^{-6} torr. All mixes were made in gaseous form before liquifaction, and in runs requiring changes of concentration we always worked from low to high levels. All spectra presented are single-shot exposures, but only in the very lowest (sub-ppm) mixtures did we see any evidence of repeated shots depleting the donors.

Observations

Rare gas dimers

In Figure 2 we show the emission spectra of the three rare-gas dimers, Ar_2, Kr_2, and Xe_2. For the spectra shown, the Kr and the Xe were in solution at concentrations of 10% and 0.01%, respectively. The low Xe level was chosen to show an accompanying atomic Xe peak which quenched out at higher concentrations. The maximum photodiode signals observed from these three species (with constant conditions and nearly constant photodiode response over these wavelengths) were 60 mV for the Ar_2, 2.8 V for the Kr_2, and 6.0 V for the Xe_2. The peaks were red-shifted by 2-3 nm from their gaseous wavelengths.

Argon/donor binary mixtures

Figure 3 shows the ArO peak generated by 100 ppb of N_2O in Ar (the N_2O donor was more effective than O_2, and became our standard oxygen donor). This peak could still be detected with less than 10 ppb of oxygen donor in the system. The ArO transition, and that of KrO, are almost identical to the oxygen green auroral transition itself, and all occur at 558 nm.[6] (XeO, however, will be seen to be more strongly bound.) The ArO peak was quite bright and, curiously, increased strongly when the liquid mixture was solidified.

The formation of trimers is expected to occur in high concentrations of the noble gas components. In agreement with this prediction, donors of F and Cl in pure liquid Ar produced only trimer excimers (in addition to Ar_2). Figures 4 and 5 show the resultant Ar_2F and Ar_2Cl (we preferred NF_3 over F_2, being as effective as fluorine donor but much easier to handle). These broad peaks were both red-shifted from their gaseous central wavelengths of 285 and 245 nm by 20 nm. Note that upon solidification the red shift increased.

Krypton plus donor in argon

These families of mixes were the least successful of our excimer-producing liquids, forming strong Kr_2 and weak peaks attributed to KrF, KrCl, Kr_2F, and KrO.

Xenon plus donor in argon

All three donors produced bright fluorescence, once the proper relative concentrations were found. The data shown were taken with Xe/donor ratios of 1/1. Figure 6 shows the emission from XeO. In contrast to ArO, XeO shows definite band structure, with the wavelength-labeled peaks coming from the 2-0 to 7-0 transitions. The two rightmost peaks are from higher levels. The mixture contained 10 ppm of both Xe and N_2O.

The donors NF_3 and Freon-11 produced complete sequences of XeF and XeCl, as shown in Figure 7. The large red shifts are evident in the (B-X) transitions, which are the normal lasing transitions. In gas lasers these occur at 308 nm (XeCl) and 352 nm (XeF), but in liquid Ar we saw these (B-X) transitions shifted to 352 and 405 nm. The concentrations were 10 ppm for the NF_3/Xe run and 100 ppm for the FR-11/Xe data.

Conclusions

Our primary question is how the density of potential lasing states in the liquids compares to those in gas excimer lasers, which we can at this time answer to a first approximation. The density of excited states approaches 10^{16} cm^{-3} in high-pressure excimer lasers.[7] Since the density of the argon host is 2×10^{22} cm^{-3}, excited-state should occur at donor concentrations on the order of 1 ppm. Most of these excimer systems, especially the xenon-based ones, fluoresced well at levels of 100 ppm or more. Thus if the kinetics and efficiencies of formation are favorable, the prospects for developing compact lasers are good.

The efficacy of the various excimers produced so far cannot be weighed on the basis of fluorescence alone. Kinetic measurements and modeling will be required to assess the best lasing candidates. The long pulse of the present e-beam machine obscures short-lifetime data. We hope to obtain a short-pulse (2-ns) Febetron for lifetime measurements, and to also extend the scope of the investigation of new excimer systems.

References

1. C. K. Rhodes, ed., Excimer Lasers (Topics in Applied Physics, Vol. 30, Second Edition, Springer-Verlag, 1984).

2. H. Jara, P. Pummer, H. Egger, and C. K. Rhodes, "Optical Properties of Rare Gas Fluoride Dimers and Trimers Dissolved in Liquid Rare Gases," Phys. Rev. B., in press.

3. A modified Hewlett-Packard Model 43710A.
4. Tracor Northern TN-1710 mainframe and Optical Spectrometer module with vuv-adapted intensified and time-gated 512-element diode array detector.
5. Matheson Hydrox Purifier Model 8301.
6. G. Black, R. L. Sharpless, and D. C. Lorents, "Production and properties of O(1S) in liquid argon (88 K) and nitrogen (77 K)," J. Chem. Phys. 72, 484 (1980).
7. M. McCusker, "The Rare Gas Excimers," in Excimer Lasers, ed. C. K. Rhodes (Topics in Applied Physics Vol. 30, Second Edition, Springer-Verlag, 1984) p. 47.

Figure 1. A schematic of the cryogenic optical cell and diagnostic train, viewed in cross-section from above. Basically, fluorescence from the irradiated liquid was collimated and propagated into an evacuated spectrometer, where an intensified diode array was used to detect the time-integrated spectrum.

Figure 2. The noble gas dimer spectra as seen in pure Ar, 100% Kr/Ar, and 0.01% Xe/Ar.

Figure 3. ArO formed in a 100 ppb solution of N_2O in Ar.

Figure 4. The halogen donors in Ar alone resulted in trimer excimers, as the Ar_2F seen here produced by 50 ppm of F_2.

Figure 5. The Cl-donating Freon-11 at 1 ppm in Ar produced Ar_2Cl. The additional red shift in a solid matrix is also shown.

Figure 6. Unlike ArO and KrO, XeO is a real bound molecule. The spectrum seen here shows a typical molecular progression of bands in the green. This spectrum was taken with a mixture of N_2O/Xe/Ar, with the N_2O and Xe present at 1 ppm in the Ar host.

Figure 7. Ternary mixtures of (1:1) Donor:Xe in Ar, with NF_3 (10 ppm) and Freon-11 (100 ppm) donors resulted in these complete series of XeF and XeCl transitions. The (B-X) are the normal lasing transitions. The (C-A) are quite broad because of the curvature of the repulsive A states.

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LIQUID EXCIMER DETECTION

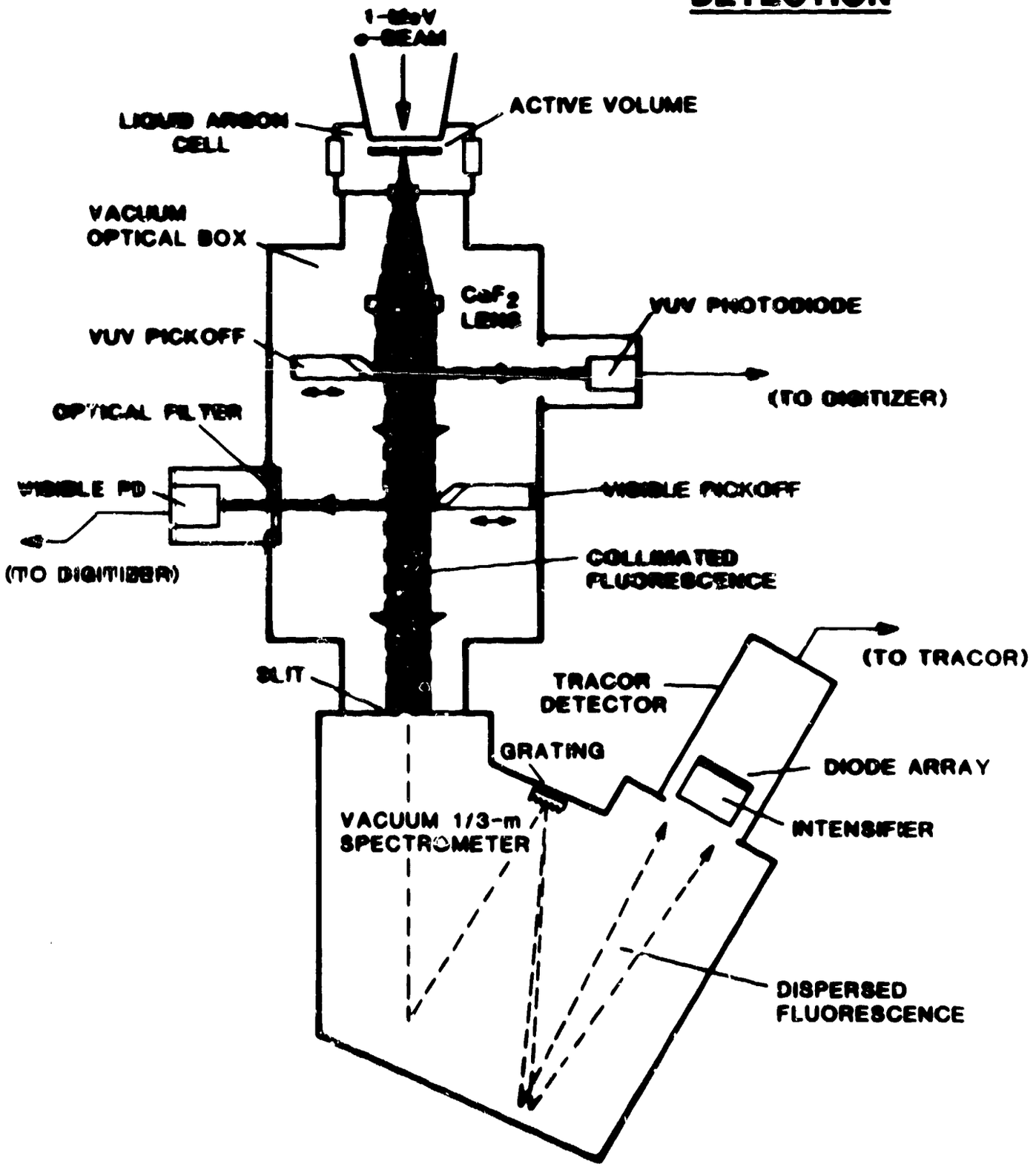


Figura 1

CHM-VG-6549

NOBLE GAS DIMERS

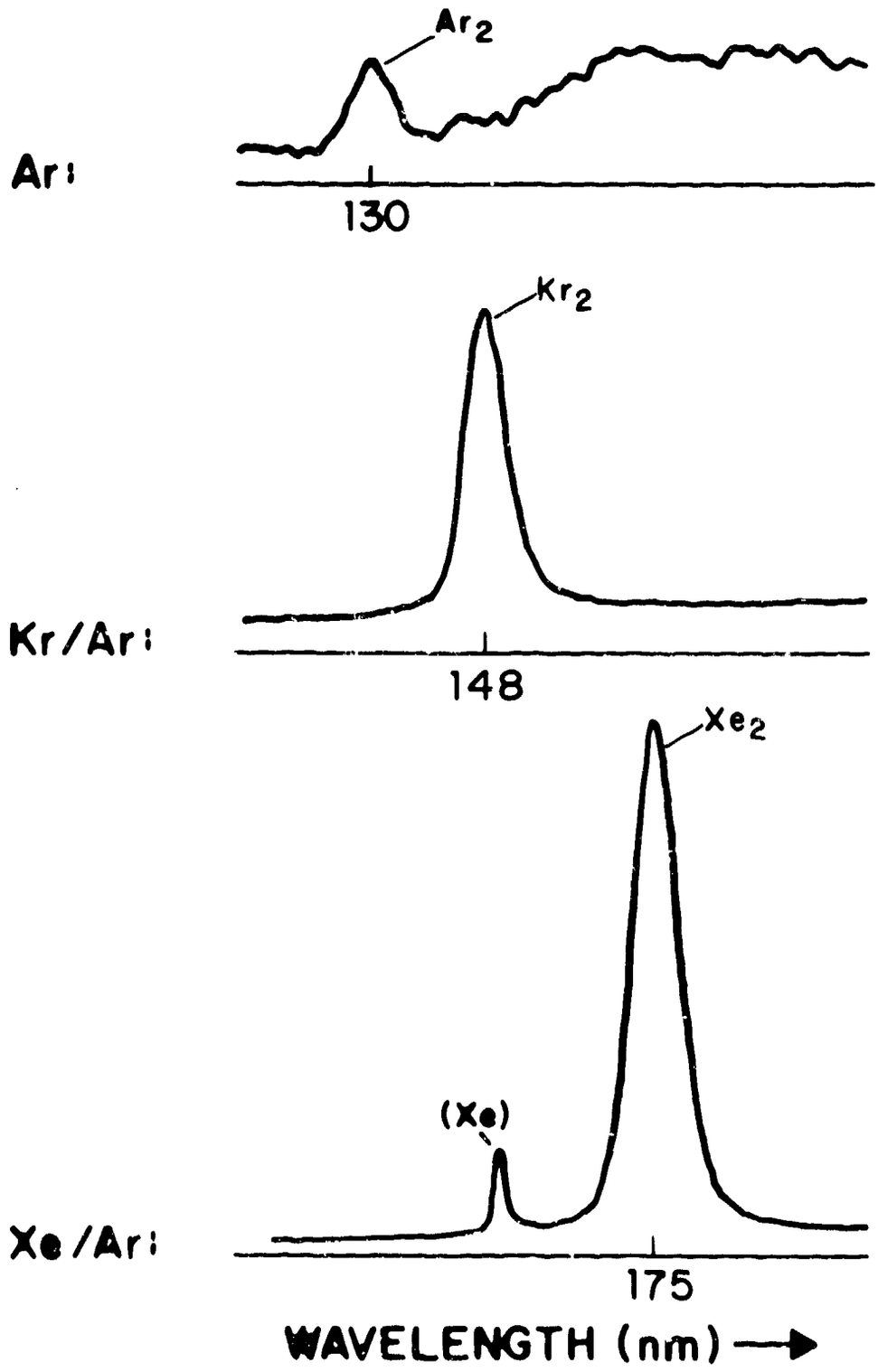


Figure 2

CHM-VG-7318

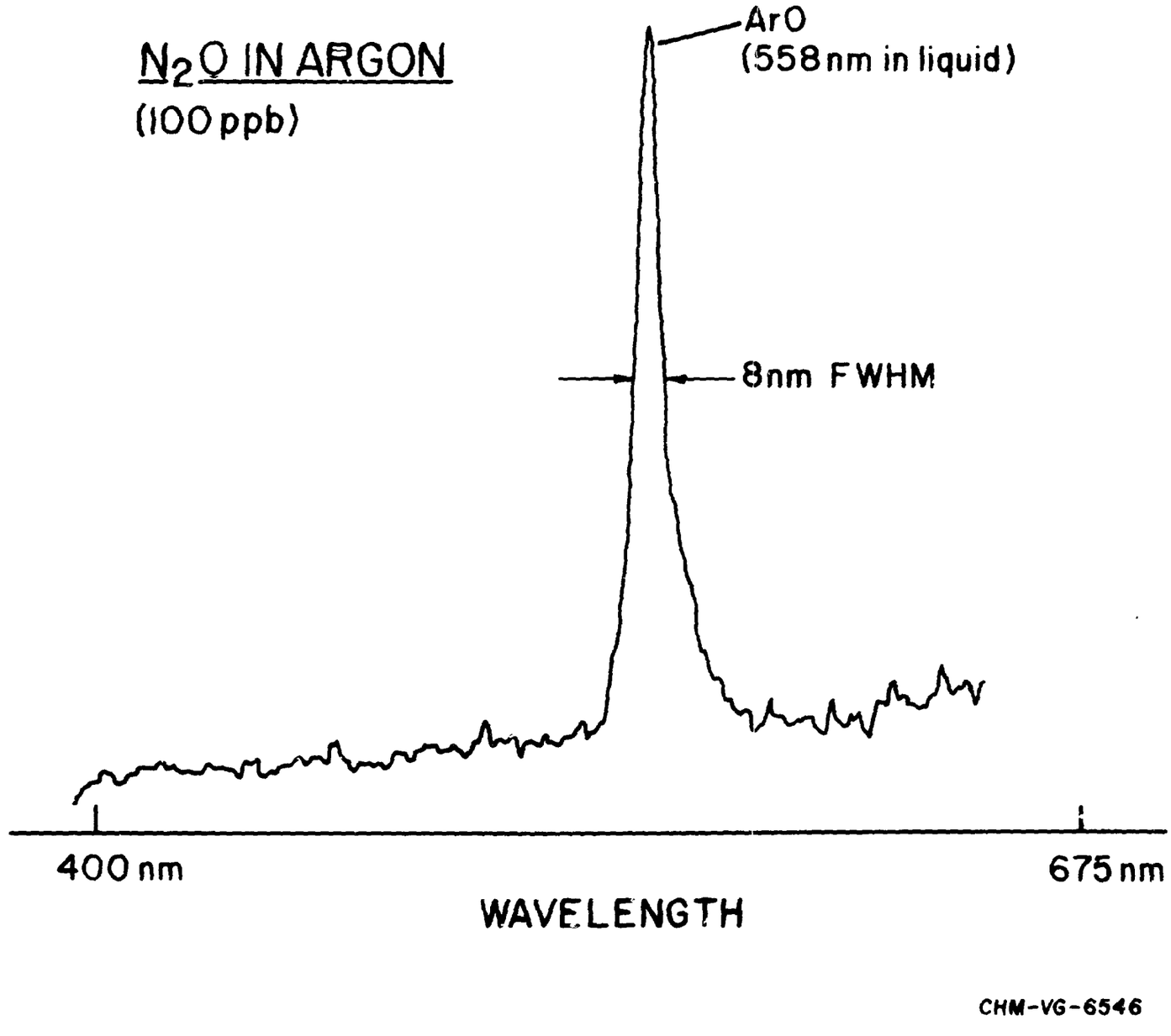
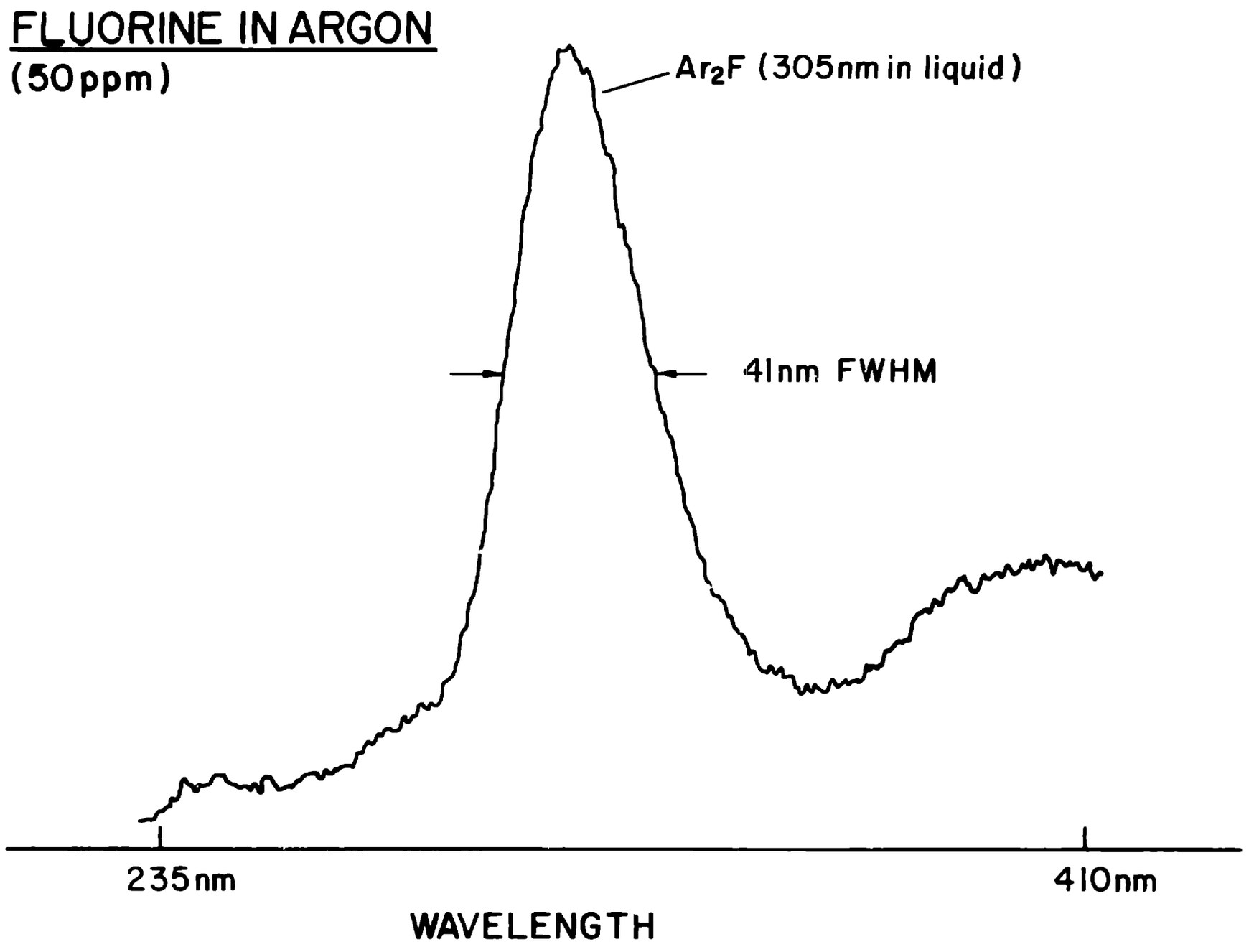
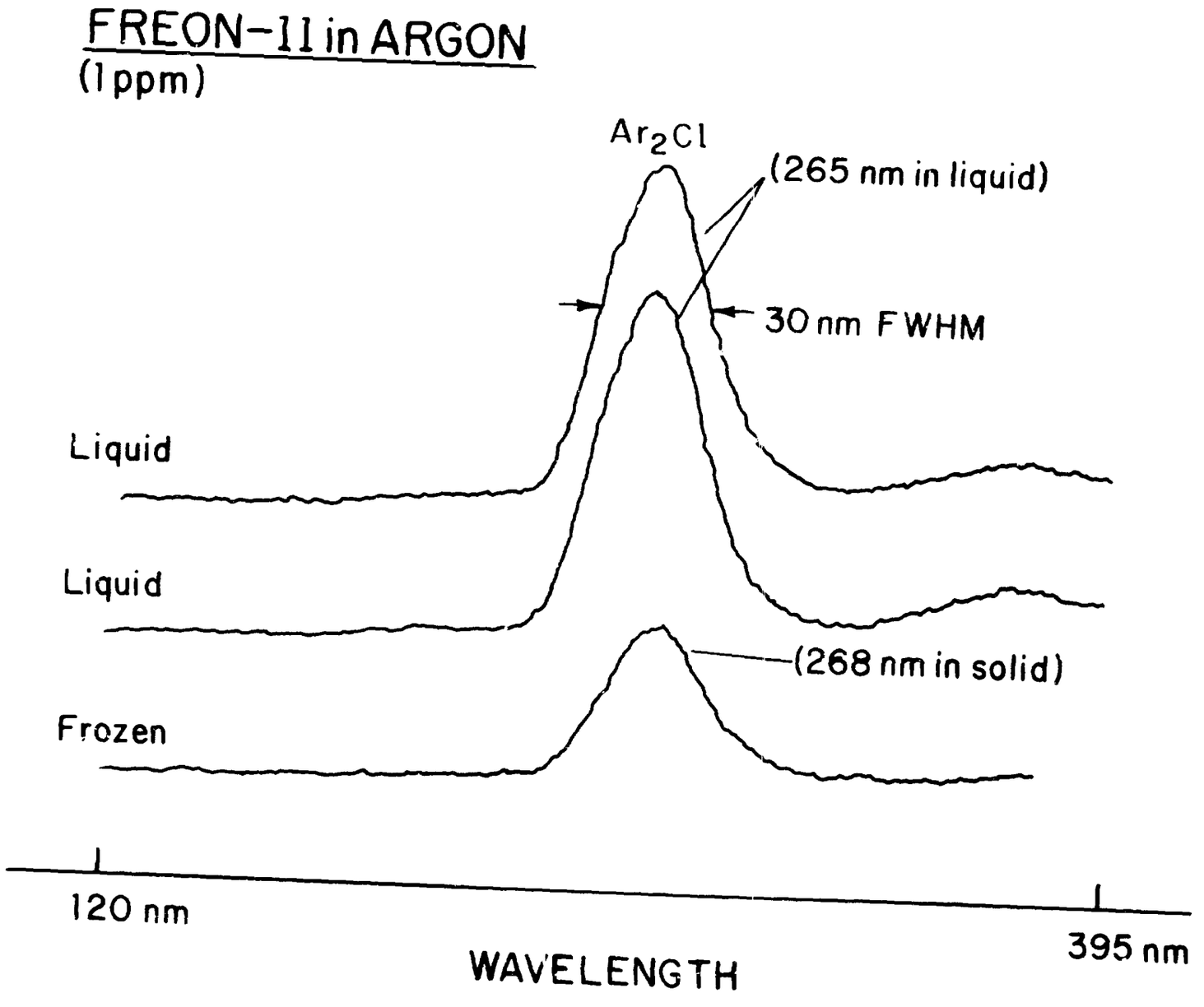

N_2O IN ARGON
(100 ppb)
ArO
(558 nm in liquid)
8nm FWHM
400 nm
675 nm
WAVELENGTH
CHM-VG-6546

Figure 3

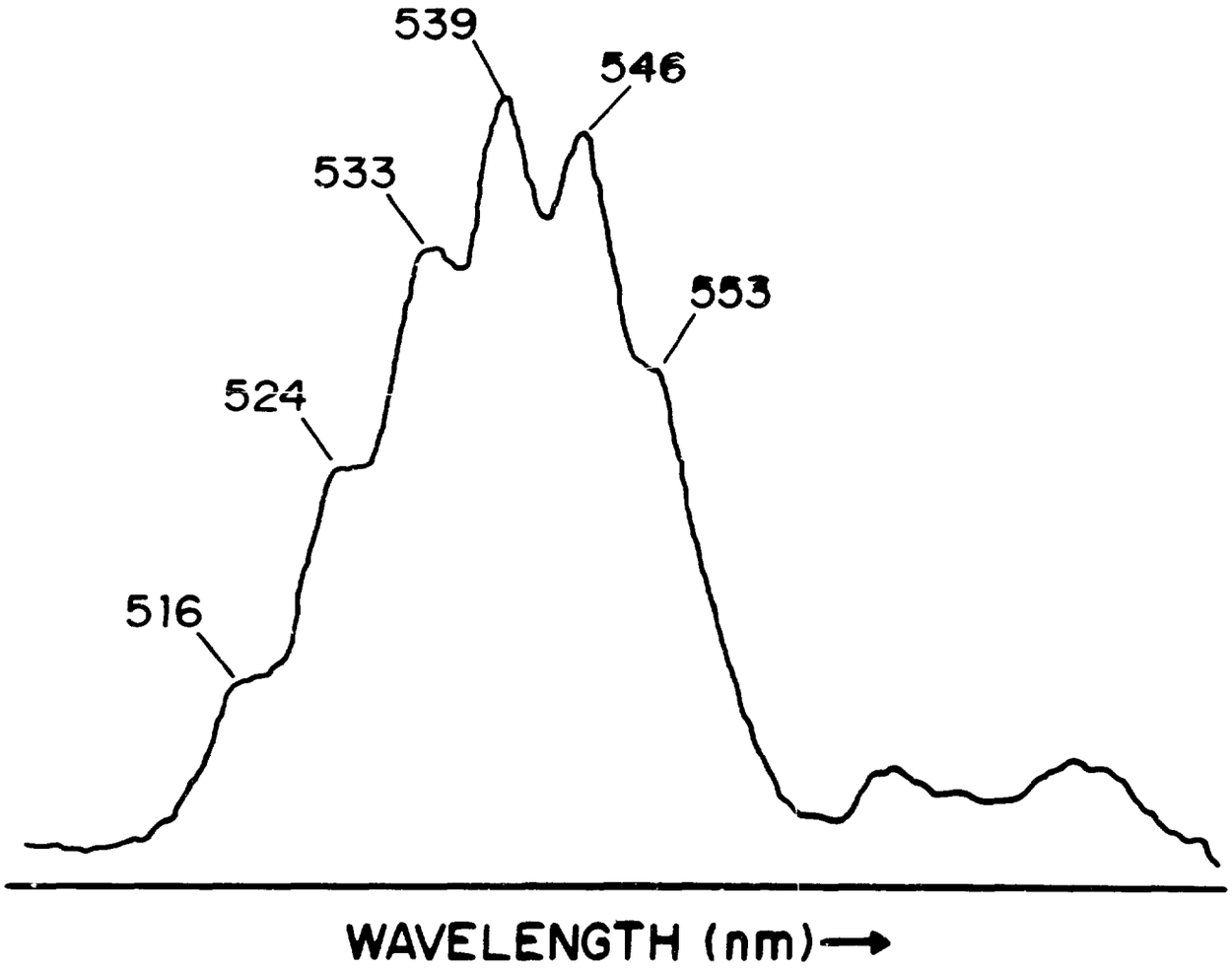

FLUORINE IN ARGON
(50ppm)
Ar_2F (305nm in liquid)
41nm FWHM
235nm
410nm
WAVELENGTH
CHM-VG-6542



CHM-VG-6547

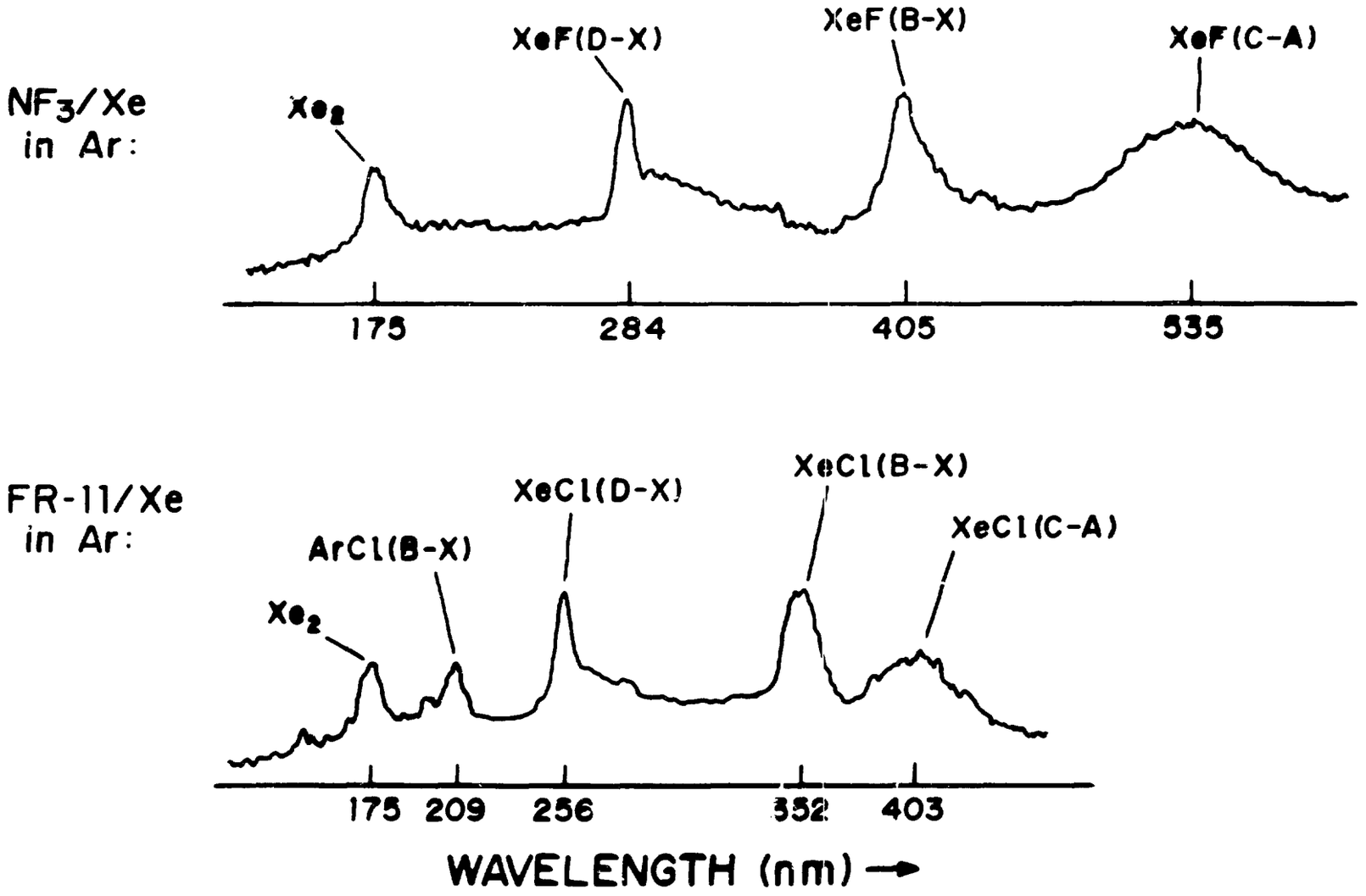
Figure 5

XeO SEQUENCE



CHM-VG-7314

Xe EXCIMER SERIES



CHM-VG-7315